Research Journal of Chemical Sciences ____ISSN 2231-606X
Vol. **14(3),** 25-32, October **(2024)** *Res. J. Chem. Sci.*

DFT Assisted Design, Generation and Spectroscopic Characterization of Hybrid Dicyclopentadienyltitanium (IV) Formulations

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Available online at: www.isca.in, www.isca.me
Received 08th July 2024, revised 14th September 2024, accepted 13rd October 2024

Abstract

New hybrid dicyclopentadienyltitanium(IV) complexes having the formulas Cp_2TiL_1L' *and* Cp_2TiL_2L'*were generated by the reactions of titanocene(IV) dichloride with sterically hindered pyrazolones [**LH**,* $\mathrm{RCO\overline{C:C(OH)N(C_6H_5)N:C}CH_3}$ *where R= -*CH_2CH_3*(**L_1H**), p-*ClC_6H_4*-(**L_2H**)] and phenoxyacetic acid (**L'H**,* $C_6H_5OCH_2$*-COOH) in the presence of triethylamine in a 1:1:1:2 molar ratio in refluxing dry THF. The structural characteristics of newly synthesized hybrid titanocene(IV)complexes were determined using analytical methods, mass spectrometry, and spectroscopic (IR,* ^1H *and* ^{13}C *NMR) techniques. On the basis of obtained evidences a hexa coordinated geometry around the titanium centre has been suggested for newly generated hybrid dicyclopentadienyltitanium(IV) complexes. DFT calculations were performed to study the electronic properties and optimized geometries of the newly prepared hybrid dicyclopentadienyltitanium(IV) formulations.*

Keywords: Titanium(IV) complexes,Titanocene(IV) dichloride, Sterically hindered pyrazolones, Phenoxyacetic acid, DFT.

Introduction

Titanium(IV) complexes generated from different organic ligands have gained attention from researchers due to their remarkable structural diversity[1] and multifaceted applications[2]. Titanium(IV) and titanocene(IV) complexes have been intensively studied for their significant biological activities, such as antibacterial[3–5], antifungal[6,7], antioxidant[8], anti-inflammatory[9] and potential cytotoxic[10–13] properties. These complexes have also found interesting applications in catalysis[14], alkene polymerization[15–17], synthetic chemistry[9], and the development of novel materials[18]. The improved characteristics, industrial uses[19] and biological[20–22] significance of hybrid materials have resulted in substantial developments in the field of material science. Hybrid dicyclopentadienyl titanium(IV) complexes have become an integral part of material science and their structure can be elucidated using analytical, spectroscopic studies[23,24], theoretical calculations based on density functional theory[25] and single-crystal structure analysis[26,27].

Sterically hindered pyrazolones are potential organic ligands. They show interesting coordinating behaviour, distinct bonding modes, fascinating structural topologies and promising biological activities of their metal complexes[28–31]. Carboxylic acids can bind to various metals and these metal carboxylates exhibit unique structural patterns[32] and hold biological significance[28,33].

The generation of hybrid titanocene(IV) complexes using sterically hindered pyrazolones and phenoxyacetic acid has not been studied. In continuation of our previous research work[4,5,23,28-31], the present work includes synthesis, spectroscopic investigation, mass study and DFT calculations of titanocene(IV) complexes derived from sterically hindered pyrazolones and phenoxyacetic acid.

Material and Methods

Phenoxyacetic acid (L'H) and titanocene dichloride were commercially available and obtained from Alfa Aesar and Sigma Aldrich, respectively. Sterically hindered pyrazolones were synthesized in the laboratory by employing Jensen's method[34]. Standard described methods were employed to dry the solvents used in the synthetic procedures. Throughout the entire synthetic process, strict anhydrous conditions were maintained. The mixture of chloroform and n-hexane was used to recrystallize the crude coloured solid products. Titanium was estimated as titanium oxide. Melting points of newly synthesized complexes were determined in sealed capillaries. IR spectra of the Cp_2TiL_1L' (complex 1**)** and Cp_2TiL_2L'(complex 2**)** were recorded on a Perkin Elmer Spectrum RX-IFTIR using KBr discs in the range 4000–400cm^{-1} and ^1H, ^{13}C NMR spectra were recorded on ECS400 MHz (JEOL) NMR Spectrometer. Mass study of complex 2 was carried out on Xevo G2-S Q (T of WATERS, USA) mass spectrometer.

Similar synthetic procedure was employed for the generation of both the titanocene(IV) complexes. Procedure for the synthesis of the representative complex-1 (Cp_2TiL_1L') is discussed in detail. The physical and analytical attributes of synthesized titanocene(IV) complexes are summarized in Table-1.

Synthesis of $Cp_2Ti[CH_3CH_2COC{:}C(O)N(C_6H_5)N{:}CCH_3][OOCCH_2OC_6H_5]$, Cp_2TiL_1L' (complex **1**)

A THF solution of 4-propionyl-2,4-dihydro-5-methyl-2phenyl-3H-pyrazol-3-one (L_1H) (0.571g, 1.55mmol) and phenoxyacetic acid (L'H) (0.2361g, 1.55 mmol) was mixed with THF solution of triethylamine (0.3140g, 3.10mmol) and stirred for 30 minutes. A dry THF solution of titanocene(IV) dichloride (0.3861g, 1.55mmol) was added dropwise to the mixture of sterically hindered pyrazolone, phenoxyacetic acid and triethylamine, the mixture content was refluxed for approximately 8 hours. Solid triethylamine hydrochloride so formed in the reaction was filtered out and excess solvent was removed under reduced pressure. Orange-red coloured solid crude product was obtained which was further purified by recrystallization from chloroform-n-hexane mixture.

Results and Discussion

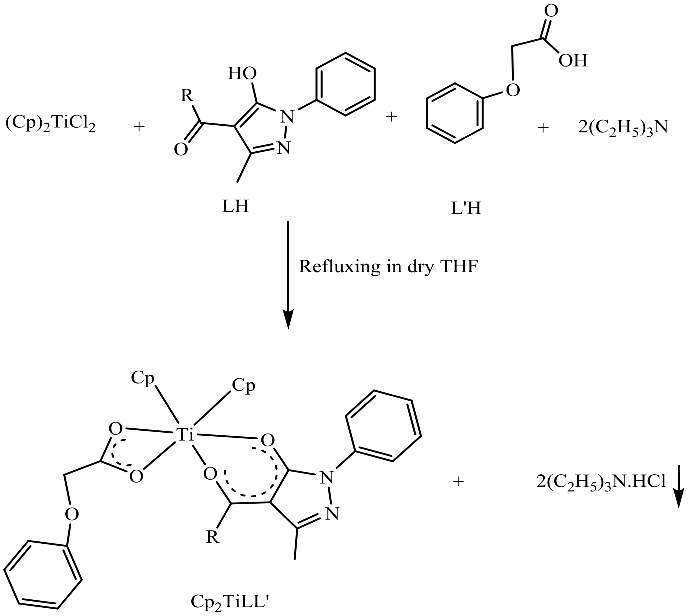
Titanocene(IV) complexes (1 and 2) were synthesized by the reactions of sterically hindered pyrazolones (LH), phenoxyacetic acid (L'H) and titanocene(IV) dichloride in the presence of triethylamine in a 1:1:1:2 molar ratio in refluxing dry THF (Scheme-1). Solid triethylamine hydrochloride formed during the course of the reaction was filtered out. The volatile solvent fraction of remaining reaction mixture was removed in vacuo to obtain crude solid products. Obtained coloured solid products were recrystallized from a mixture of chloroform and n-hexane.

The tentative structures of titanocene(IV) complexes (1 and 2) were elucidated using vibrational (IR), nuclear magnetic resonance (^1H and ^{13}C) spectroscopy and mass spectrometry.

Table-1: Physical and analytical data of titanocene(IV) complexes of sterically hindered pyrazolones and phenoxyacetic acid.

Complex Number Complex formula	Reagents in g (mmol)				$Et_3N.HCl$ Found (Calc.)	% Yield* Colour	Melting point (°C)	% Ti Found (Calc.)
	Et_3N	L'H	L_1H/ L_2H	Cp_2TiCl_2				
Complex **1** Cp_2TiL_1L' $Cp_2Ti[CH_3CH_2COC{:}C(O)N(C_6H_5)N{:}CCH_3][OOCCH_2OC_6H_5]$	0.3140 (3.10)	0.2361 (1.55)	0.3571 (1.55)	0.3861 (1.55)	0.4270 (0.4271)	63 Orange red	90	8.57 (8.51)
Complex **2** Cp_2TiL_2L' $Cp_2Ti[p\text{-}ClC_6H_4COC{:}C(O)N(C_6H_5)N{:}CCH_3][OOCCH_2OC_6H_5]$	0.3061 (3.02)	0.2302 (1.51)	0.4731 (1.51)	0.3771 (1.51)	0.4176 (0.4176)	65 Yellow orange	110	7.41 (7.47)

*= yield of recrystallized product



Scheme-1: Synthesis of new dicyclopentadienyltitanium(IV) complexes of sterically hindered pyrazolones(LH) and phenoxyaceticacid (L'H). Where; R = $-CH_2CH_3$. Cp_2TiL_1L' (Complex 1). R = $p\text{-}ClC_6H_4$-Cp_2TiL_2L' (Complex 2).

IR spectra: The IR spectra of titanocene(IV) complexes of sterically hindered pyrazolones and phenoxyacetic acid (1 and 2) were recorded as KBr discs in the range of 4000 – 400 cm^{-1}.

Titanocene(IV) complexes, Cp_2TiL_1L' and Cp_2TiL_2L' showed new medium intensity absorption bands at 689cm^{-1}, 495cm^{-1} and 624cm^{-1}, 505cm^{-1}, respectively in their IR spectra. These bands may be attributed to Ti-O bond stretching vibrations[23]. Absorption bands observed at 449cm^{-1} in the infrared spectrum of complex 2 may be ascribed to stretching vibrations of the Ti-Cp ring[23]. A band at 1545 cm^{-1} was seen in the infrared spectra of sterically hindered pyrazolones[35] (L_1H and L_2H), which may be related to carbonyl ν(>C=O) stretching vibrations. The synthesized titanocene(IV) complexes showed this band at 1495 cm^{-1} in complex 1 and at 1525 cm^{-1} in complex 2. The shift in the position of ν(>C=O) stretching vibrations towards a lower wave number indicates that these ligands are behaving bidentately and the coordination is occurring through the carbonyl oxygen[23,35]. Absorption bands due to $\nu(-C_6H_5)$ appeared in the IR spectra of these complexes in the region of 1594–1591 cm^{-1}.

Titanocene(IV) complexes of type Cp_2TiLL' were synthesized using phenoxyacetic acid (L'H) as a co-ligand. The IR spectra of complexes showed the absorption bands corresponding to the stretching vibrations of $\nu\ (COO)_{asym}$ and $\nu\ (COO)_{sym}$ at 1700cm^{-1} 1495 cm^{-1} in complex 1 and 1701 cm^{-1}, 1471 cm^{-1} in complex 2. The nature of bonding of carboxylate (COO^-) ligand in these complexes may be studied by calculating $\Delta\nu[\Delta\nu = \nu(COO)_{asym} - \nu(COO)_{sym}]$. The calculated values of Δν were 205 and 230 cm^{-1} in IR spectra of complexes 1 and 2, respectively. The obtained value of Δν indicates the chelating bidentate mode of bonding of the carboxylate ligand (L'H) in newly prepared titanocene(IV)complexes[29,36]. The medium intensity bands appeared in the region1326–1306 cm^{-1} for C-C stretching vibrations. The C-H bending vibration[23] bands were noted in the regions 1094–1083cm^{-1} (in plane bending) and 834–791cm^{-1} (out of plane bending) in the spectra of titanocene(IV) complexes. These vibrations suggest the η^5 bonding mode of cyclopentadienyl rings in these complexes.

^{1}H NMR spectra: Titanocene(IV) complexes were characterized by recording their ^{1}H NMR spectra in $CDCl_3$ solvent with TMS serving as an internal standard. Table-2 lists the observed proton signals of pyrazolones[35] (L_1H, L_2H), phenoxyacetic acid (L'H) and their corresponding titanocene(IV) complexes (Cp_2TiL_1L', Cp_2TiL_2L').

The enolic -OH of sterically hindered pyrazolones and carboxylic -COOH of phenoxyacetic acid appeared as a broad singlet peak at δ 10.67ppm (L_1H), at δ 11.37ppm (L_2H) and at δ 10.92ppm (L'H), in ^{1}H NMR spectra. The deprotonation of these ligands is established by the absence of these broad signals (caused by enolic –OH and carboxylic –COOH) in the ^{1}H NMR spectra of the titanocene(IV) complexes (**1** and **2**).

The ring methyl protons ($-CH_3$) of the sterically hindered pyrazolones (LH) moiety are observed as a singlet at δ 1.32ppm (1) and at δ 1.25ppm (2) whereas the methylene proton signals detected at δ 4.22 and 4.60ppm in the ^{1}H NMR spectra of complex 1 and complex 2, respectively. The ^{1}H NMR spectra of these newly synthesized complexes demonstrated a complex pattern in the range of δ 6.67–7.27ppm due to aromatic protons. The ^{1}H NMR spectra of the complexes revealed a broad singlet due to the protons of the cyclopentadienyl at δ 6.37ppm in complex 1 and at δ 6.41ppm in complex 2.

Table-2: ^{1}H NMR signals of sterically hindered pyrazolones, phenoxyacetic acid and their corresponding titanocene(IV) complexes in (δ) ppm.

Ligand/ Complex	$RCOC:C(OH)N(C_6H_5)N:CCH_3$ (LH)				$C_6H_5OCH_2$-COOH (L'H)			$(C_5H_5)_2Ti$
	OH	Ring C_6H_5	Ring CH_3	Terminal R CH_2CH_3 / p-ClC_6H_4-	COO-H	CH_2	C_6H_5	
L_1H^a	10.67 (bs)	7.23-7.86(m)	2.39 (s)	1.21(t), 2.73 (q)				
L_2H^a	11.37 (bs)	7.26-8.00(m)	2.14 (s)	*				
L'H					10.92 (s)	4.68 (s)	6.91-7.31 (m)	
Complex 1 Cp_2TiL_1L'	-	6.88-7.27 (m)	1.32 (s)	2.46 (q),un 1.34 (t),un	-	4.60 (s)	*	6.37 (b)
Complex 2 Cp_2TiL_2L'	-	6.67-7.12 (m)	1.25 (s)	*	-	4.22 (s)	*	6.41 (b)

* merged with ring phenyl region; b= broad, s=singlet, t=triplet, q=quartet, m=multiplet, un=unresolved; a=ref. 35

^{13}C NMR spectra: The ^{13}C NMR spectra of phenoxyacetic acid and titanocene(IV) complexes were recorded in $CDCl_3$ solvent. Table-3 lists the observed chemical shift values of the distinctive carbons of pyrazolones[35] (L_1H, L_2H), phenoxyacetic acid (L'H) and their corresponding titanocene(IV) complexes (Cp_2TiL_1L', Cp_2TiL_2L').

Important evidences for the formation of titanocene(IV) complexes were provided by the ^{13}C NMR spectra. The ^{13}C NMR spectra of ligands L_1H and L_2H showed the carbonyl (>C=O) carbon signal at δ 197.97 and δ 190.9ppm, respectively. This carbonyl (>C=O) group is involved in bonding, as evidenced by the noticeable shift in the position of carbonyl carbon signals in the ^{13}C NMR spectra of newly synthesized titanocene (IV) complexes. The ^{13}C NMR spectra of titanocene (IV) complexes displayed a shift in the positions of the ring carbon signals relative to their positions in the parent ligands L_1H and L_2H.

The carboxylic carbon signals were detected at δ 171.6ppm in complex 1 and at δ 181.0ppm in complex 2 in the ^{13}C NMR spectra of the complexes (Table-3). The bidentate behaviour of carboxylic group of phenoxyacetic acid (L'H) in titanocene(IV) complexes is indicated by the shift in the position of carboxylic carbon signals in the ^{13}C NMR spectra of complexes. In the ^{13}C NMR spectra of the complexes, the carbon signal of the >CH_2 group in phenoxyacetic acid (L'H) also showed some downfield shift in relation to its position in the free ligand. The ^{13}C NMR spectra of titanocene(IV) complexes showed aromatic carbon signals in the range of δ119.5–157.7ppm. The appearance of signals in the region δ 114.7-114.8ppm was due to cyclopentadienyl group attached to the titanium atom.

Mass spectrometry: Time of Flight-Mass Spectrometry (TOF-MS) method was used to obtain the mass spectral information of one of the representative titanocene(IV) complex, Cp_2TiL_2L' (Complex-2). Table-4 presents mass fragmentation data of complex including m/z values and % intensity. The molecular ion peak (M^+), was not observed in the mass spectrum of the titanocene(IV) complex. The mass spectrum of the complex 2 also showed a few fainter peaks for higher molecular weight ions due to recombination of various fragment ions.

Table-3: ^{13}C NMR signals of sterically hindered pyrazolones, phenoxyacetic acid and their corresponding titanocene(IV) complexes in (δ) ppm.

Ligand/ Complex	C_6H_5	RCOC:C(OH)N(C_6H_5)N:CCH$_3$ (LH)						$C_6H_5OCH_2$-COOH (L'H)		$(Cp)_2Ti$
		Terminal R CH_2CH_3/ p-ClC_6H_4	C3	C4	C5	C6	C7	COOH	CH_2	
L_1H^a	120.40,128.88, 129.15,147.32	7.94, 32.29	160.10	103.27	137.06	197.97	15.48			
L_2H^a	120.8,128.8,129.1, 147.6	126.8,129.0, 136.2,138.0	161.1	103.5	138.1	190.9	15.8			
L'H	114.7,122.1,129.8, 157.4							175.1	64.8	
Complex 1 Cp_2TiL_1L'	129.1-157.7	31.5,8.7	165.3	102.3	138.4	191.2	16.7	171.6	65.1	114.8
Complex 2 Cp_2TiL_2L'	119.5-157.5	*	157.5	101.9	137.5	191.6	16.2	181.0	65.0	114.7

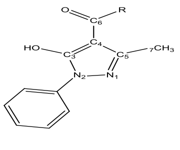
*merged with phenyl ring; LH=  where R=-CH_2CH_3 (L_1H), p-ClC_6H_4- (L_2H); a=ref. 35

Table-4: Mass fragmentation pattern of titanocene(IV) complex, Cp_2TiL_2L'(Complex 2).

Fragment ion	m/z Observed (Calc.)	% Intensity
$[C_{35}H_{29}N_2O_5ClTi]^{+\cdot}$	Not Observed (640.93)	
$[C_{29}H_{24}N_2O_5ClTi]^{+\cdot}$	565.81 (563)	11.36
$[C_{22}H_{13}N_2O_2ClTi]^{+\cdot}$	420.97 (420)	100
$[C_{17}H_{13}N_2O_2Cl+H]^{+\cdot}$	313.02 (312)	28.40
$[C_5H_3N_2O_2Ti-H]^{+\cdot}$	168.99 (170)	23.29
$[C_5H_{10}O_2]^{+\cdot}$	102.13 (102)	11.36

A hexa-coordinated geometry for the titanocene(IV) complexes of sterically hindered pyrazolones and phenoxyacetic acid was proposed by analysis of the data from vibrational (IR), nuclear magnetic resonance (^{1}H and^{13}C), and mass spectrometry (Figure-1).

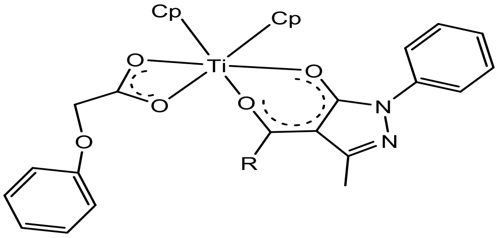


Figure-1: Tentative structure of titanocene(IV) complexes of sterically hindered pyrazolones and phenoxyacetic acid.
Where: R = $-CH_2CH_3$, Cp_2TiL_1L' (Complex 1), R = p-ClC_6H_4- Cp_2TiL_2L' (Complex 2)

Theoretical calculations: To obtain insight into the optimized molecular structures, geometries, energies and reactivity descriptors, DFT calculations of newly synthesized hybrid titanocene(IV) complexes (Cp_2TiL_1L', Cp_2TiL_2L') have been performed utilizing the B3LYP/6-31G* basis set. The obtained energies, electronic properties and global reactivity descriptors are listed in Table-5.

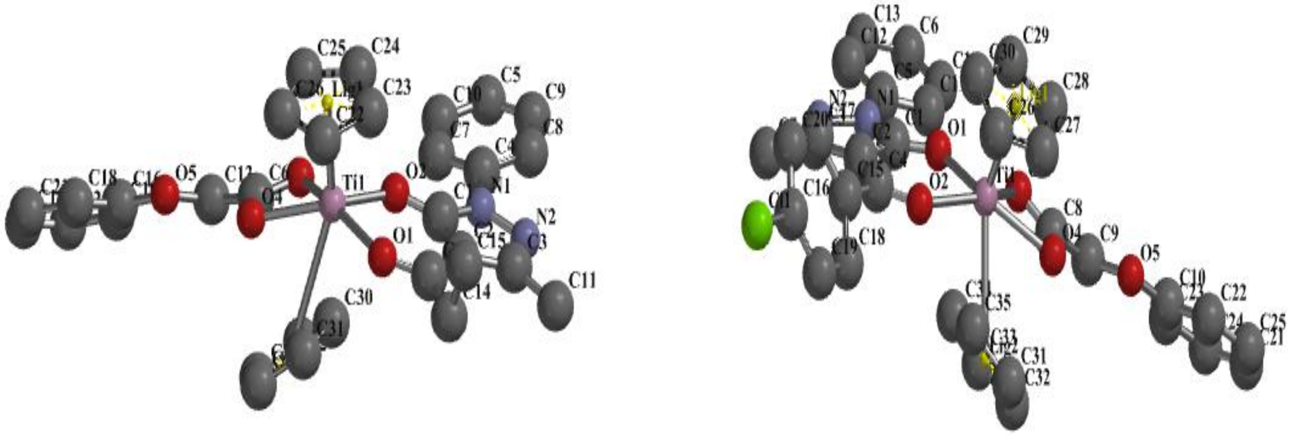
The ground state energies of the optimized geometries of L_1H[37] and L_2H[37] are -763.770345au and -1375.78582au, respectively whereas the ground state energies of the optimized geometries of their corresponding complexes are -2534.50056au (Cp_2TiL_1L') and -3146.51627au (Cp_2TiL_2L'). These results indicate towards the increased stability of titanocene(IV) complexes relative to their parent ligands[29]. The energy gap (ΔE_{gap}) of ligands was found 4.99eV in L_1H, and 4.36eV in L_2H. In the newly synthesized titanocene(IV) complexes, obtained energy gap (ΔE_{gap}) values are 2.59eV in Cp_2TiL_1L' and 2.96eV in Cp_2TiL_2L'. The lowering in HOMO-LUMO energy gap value (ΔE_{gap}) of newly synthesized titanocene(IV) complexes implied towards their increased reactivity.

Table-5: Global reactivity descriptors obtained from DFT calculations of titanocene(IV) complexes.

Properties	Cp_2TiL_1L' (complex 1)	Cp_2TiL_2L' (complex 2)
Molecular formula	$C_{31}H_{30}N_2O_5Ti$	$C_{35}H_{29}ClN_2O_5Ti$
Molecular weight	558.495	640.985
Energy (au)	-2534.50056	-3146.51627
E_{HOMO} (eV)	-5.04	-5.44
E_{LUMO} (eV)	-2.45	-2.48
ΔE (eV)	2.59	2.96
Dipole moment(Debye)	3.29	1.51
Polarization	85.52	90.39
Ionization potential (eV)	5.04	5.44
Electron affinity (eV)	2.45	2.48
Electronegativity (χ)	3.745	3.96
Chemical potential (μ)	-3.745	-3.96
Chemical hardness (η)	1.295	1.48
Chemical softness (S)	0.3861	0.3378

[$IP = - E_{HOMO}$; $EA= - E_{LUMO}$; $\mu= -(IP+EA/2)$; $\chi= (IP+EA/2)$; $\eta= (IP-EA/2)$; $S=1/2\eta$]

The optimized geometries of the titanocene(IV) complexes were examined with respect to their bond lengths and bond angles. The structural parameters (bond lengths and bond angles) and optimized geometries of hybrid titanocene(IV) complexes are depicted in Table-6 and Figure-2. The analysis of optimized geometries indicates two unequal bond lengths of Ti-Cp in titanocene(IV) complexes. These are 2.190 Å (Ti1-Lig1) and 3.104 Å (Ti1-Lig2) in complex 1, whereas 2.162 Å (Ti1-Lig1) and 2.893 Å (Ti1-Lig2) in complex 2. The values of bond angles indicated distortion around the central Ti centre in these complexes. The obtained bond angles are 150.55° (Lig1-Ti1-Lig2) and 138.53° (Lig1-Ti1-Lig2) in complex 1 and complex 2, respectively. The presence of two unequal Ti-Cp bond lengths and distortion in geometry around Ti centre may be caused by the difference in coordination behaviour of both the ligands with Ti atom[30].



(a) Complex 1 **(b)** Complex 2

Figure-2: Optimized molecular structure of titanocene(IV) complexes.

Table-6: Selected bond lengths (in Å) and bond angles (in Å) of optimized molecular structures of titanocene(IV) complexes.

Cp_2TiL_1L' (complex 1) Bond length	Cp_2TiL_2L' (complex 2) Bond length	Cp_2TiL_1L' (complex 1) Bond angle	Cp_2TiL_2L' (complex 2) Bond angle
2.190 (Ti1-Lig1)	2.162 (Ti1-Lig1)	150.55 (Lig1-Ti1-Lig2)	138.53 (Lig1-Ti1-Lig2)
3.104 (Ti1-Lig2)	2.893 (Ti1-Lig2)	103.82 (Lig1-Ti1-O3)	106.23 (Lig1-Ti1-O3)
2.153 (Ti1-O4)	2.185 (Ti1-O3)	97.77 (Lig1-Ti1-O4)	95.85 (Lig1-Ti1-O4)
2.168 (Ti1-O3)	2.214 (Ti1-O4)	96.97 (Lig1-Ti1-O1)	94.84 (Lig1-Ti1-O2)
1.273 (O3-C6)	1.271 (O3-C8)	104.52 (Lig1-Ti1-O2)	107.10 (Lig1-Ti1-O1)
1.264 (O4=C6)	1.257 (O4=C8)	83.45 (Lig2-Ti1-O3)	92.03(Lig2-Ti1-O3)
2.014 (Ti1-O2)	2.030 (Ti1-O1)	60.56 (Lig2-Ti1-O4)	61.87(Lig2-Ti1-O4)
2.109 (Ti1-O1)	2.217 (Ti1-O2)	85.15 (Lig2-Ti1-O1)	87.01(Lig2-Ti1-O2)
1.280 (O2-C1)	1.278 (O1-C1)	104.92 (Lig2-Ti1-O2)	113.91(Lig2-Ti1-O1)
1.431 (C1=C2)	1.428 (C1=C2)	60.54 (O4-Ti1-O3)	59.12(O4-Ti1-O3)
1.412 (C2-C12)	1.412 (C2-C4)	77.40 (O3-Ti1-O2)	72.36(O3-Ti1-O1)
1.272 (C12=O1)	1.269 (C4=O2)	84.27 (O2-Ti1-O1)	79.35(O1-Ti1-O2)
		130.27 (O4-Ti1-O1)	142.59(O2-Ti1-O4)

Conclusion

In this research work, titanocene dichloride reacted with sterically hindered pyrazolones and carboxylic acid to form new hybrid titanocene(IV) complexes. On the basis of mass spectrometry, spectroscopic, and physico-chemical data, plausible structures for these complexes were proposed. The spectral study analysis suggested a monomeric, hexacoordinated titanium centre with deformed geometry in titanocene(IV) complexes. These results were supported by DFT calculations of newly synthesized titanocene(IV) complexes. Two cyclopentadienyl rings and four oxygen atoms from two bidentate chelating ligands (sterically hindered pyrazolones and phenoxyacetic acid), surround the central titanium atom.

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